FORM PTO-1390 (REV 10-95)

U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. §371

ATTORNEY'S DOCKET NUMBER: TROPL 12

U.S APPLICATION NO (If known, see 37 CFR §1 5): 10/049850

INTERNATIONAL APPLICATION NO	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/DE00/02743	16 AUGUST 2000	16 AUGUST 1999

TITLE OF INVENTION: COMPOUND SAFETY GLASS AND PVB FOIL FOR THE PRODUCTION THEREOF

APPLICANT(S) FOR DO/EO/US: KELLER, Uwe, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ■ This is a **FIRST** submission of items concerning a filing under 35 U S C. §371
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. §371.
3. ☐ This express request to begin national examination procedures (35 U S.C. §371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. §371(b) and PCT Articles 22 and 39(1).
4. ■ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ■ A copy of the International Application as filed (35 U.S.C. §371(c)(2))
   a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ■ has been transmitted by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ■ A translation of the International Application into English (35 U.S.C. §371(c)(2)).
7. ■ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. §371(c)(3))
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ■ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☐ have not been made and will not be made.
8. ■ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C §371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. §371(c)(4))
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. §371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 C.F.R. §§1.97 and 1.98.
12. ☐ An assignment document for recording A separate cover sheet in compliance with 37 C F.R. §§3.28 and 3.31 is included.
13. ■ A FIRST preliminary amendment.
    ☐ A SECOND or SUBSEQUENT preliminary amendment
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter
16. ☐ Other items or information:

U.S. APPLICATION NO (if known, see 37 CFR §1.5)	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER
10/049850	PCT/DE00/02743	TROPL 12

17. ☒ The following fees are submitted:

BASIC NATIONAL FEE (37 CFR §1.492 (a) (1) - (5)):

		CALCULATIONS PTO USE ONLY
Search Report has been prepared by the EPO or JPO.....	$890.00	
International preliminary examination fee paid to USPTO (37 CFR §1.482)	$710.00	
No international preliminary examination fee paid to USPTO (37 CFR §1 482) but international search fee paid to USPTO (37 CFR §1 445(a)(2)).....	$740.00	
Neither international preliminary examination fee (37 CFR §1 482) nor international search fee (37 CFR §1.445(a)(2)) paid to USPTO	$1040.00	
International preliminary examination fee paid to USPTO (37 CFR §1.482) and all claims satisfied provisions of PCT Article 33(2)-(4).....	$100.00	

ENTER APPROPRIATE BASIC FEE AMOUNT =	$890.00	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 C.F.R. §1.492(c)).		

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	8 - 20 =	0	x $ 18.00	$0.00	
Independent claims	3 - 3 =	0	x $ 84 00	$0.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ $ 280 00		
TOTAL OF ABOVE CALCULATIONS =				$890.00	
Reduction of 1/2 for filing by small entity, if applicable. A Verified Small Entity Statement must also be					
SUBTOTAL =				$890.00	
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 C.F.R. §1.492(f)).					
TOTAL NATIONAL FEE =				$890.00	
Fee for recording the enclosed assignment (37 C.F.R. §1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 C.F.R. §§3.28, 3 31). $40.00 per property					
TOTAL FEES ENCLOSED =				$890.00	
				Amount to be refunded:	
				charged:	

a. ■ A check in the amount of $890.00 to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. 13-3402 in the amount of $ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ■ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 13-3402. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 C.F.R. §§1.494 or 1.495 has not been met, a petition to revive (37 C.F.R. §1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO: Customer Number 23,599

23599
PATENT TRADEMARK OFFICE

Filed: 19 FEBRUARY 2002
HBS:kmo

SIGNATURE

Harry B. Shubin
NAME

32,004
REGISTRATION NUMBER

IN THE UNITED STATES DESIGNATED/ELECTED OFFICE

International Application No.	:	PCT/DE00/02743
International Filing Date	:	16 AUGUST 2000
Priority Date(s) Claimed	:	16 AUGUST 1999
Applicant(s) (DO/EO/US)	:	KELLER, Uwe, et al.

Title: COMPOUND SAFETY GLASS AND PVB FOIL FOR THE PRODUCTION THEREOF

PRELIMINARY AMENDMENT

Commissioner for Patents
Washington, D.C. 20231

SIR:

Prior to calculating the national fee, and prior to examination in the National Phase of the above-identified International application, please amend as shown below. Please note that the claims of the application were amended under Article 34. This Preliminary Amendment is based on the amended claims.

IN THE CLAIMS:

3. (Amended) Laminated safety glass according to claim 1, characterized in that the proportion of the polyalkylene glycols in the total mixture for the intermediate layer is greater than 10% by weight and less than 25% by weight.

4. (Amended) Laminated safety glass according to claim 1, characterized in that at least one plasticizer selected from the group consisting of

- esters of polybasic aliphatic or aromatic acids,
- polyhydric aliphatic or aromatic alcohols or oligoehter glycols having not more than four ether units with one or more unbranched or branched aliphatic or aromatic substituents, e.g. dialkyl adipate, dialkyl sebacate, esters of di-, tri- or tetraglycols with linear or branched aliphatic

carboxylic acids
is used as further plasticizer in the plasticizer mixture.

6. (Amended) Laminated safety glass according to any of claim 1, characterized in that a polyvinyl butyral having from 19 to 22% by weight of vinyl alcohol radical and from 0.5 to 2.5% by weight of acetate radical is used as resin.

REMARKS

The purpose of this Preliminary Amendment is to eliminate multiple dependent claims in order to avoid the additional fee. Applicants reserve the right to reintroduce claims to canceled combined subject matter.

Attached hereto is a marked-up version of the changes made to the claims by the current amendment. The attached pages are captioned "**Version With Markings to Show Changes Made**".

Respectfully submitted,

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VERSION WITH MARKINGS TO SHOW CHANGES MADE

Claims 3,4 and 6 were amended as follows:

3. (Amended) Laminated safety glass according to claim 1 ~~or 2~~, characterized in that the proportion of the polyalkylene glycols in the total mixture for the intermediate layer is greater than 10% by weight and less than 25% by weight.

4. (Amended) Laminated safety glass according to ~~any of~~ claims 1 ~~to 3~~, characterized in that at least one plasticizer selected from the group consisting of

- esters of polybasic aliphatic or aromatic acids,
- polyhydric aliphatic or aromatic alcohols or oligoehter glycols having not more than four ether units with one or more unbranched or branched aliphatic or aromatic substituents, e.g. dialkyl adipate, dialkyl sebacate, esters of di-, tri- or tetraglycols with linear or branched aliphatic carboxylic acids

is used as further plasticizer in the plasticizer mixture.

6. (Amended) Laminated safety glass according to any of claims 1 ~~to 5~~, characterized in that a polyvinyl butyral having from 19 to 22% by weight of vinyl alcohol radical and from 0.5 to 2.5% by weight of acetate radical is used as resin.

Laminated safety glass and PVB film for producing the same

Technical field

The invention relates to laminated safety glass with improved acoustic properties, and also to a PVB film for producing the same. Laminated safety glass is generally composed of two panes of glass and of an adhesive film bonding the panes. The vast majority of adhesive films used are films made from plasticized, partially acetalized polyvinyl alcohols, in particular from polyvinyl butyral (PVB). Examples of use of the abovementioned laminated safety glass are windscreens in the motor vehicle sector, and also glazing in the construction sector.

The plasticizers mainly used in industry for PVB are aliphatic diesters of tri- or tetraethylene glycol. These include 3GH, 3G7, 3G8, and also 4G7, where the prefixed figure indicates the number n in the repeat unit $H-(O-CH_2-CH_2)_n-OH$ of the oligoethylene glycol fraction and H indicates 2-ethylbutyrate, 7 indicates n-heptanoate and 8 indicates 2-ethylhexanoate. Examples of other known plasticizers for polyvinyl butyral are dialkyl adipates with aliphatic or, respectively, cycloaliphatic ester components, dialkyl sebacates, triorganophosphates, triorganophosphites and phthalate plasticizers, such as benzyl butyl phthalate.

Compared with monolithic panes of glass with the same overall thickness, laminated safety glass has higher sound insulation. This is attributable to the fact that the elasticity of the PVB film reduces the mechanical coupling between the individual panes, and thus hinders the transfer of vibration from the side of the pane facing the sound source to the opposite side of the pane.

The insulation efficiency of glazing can be determined as a function of the frequency to DIN 52210 or DIN EN ISO 717, and is expressed by the sound insulation value R_w, which is a weighted average over the frequency range from 100 to 3150 Hz relevant for the acoustics of buildings. A higher value R_w here represents better sound insulation by the glazing. For example, a pane of conventional laminated glass with the structure 3 mm of glass/0.38 mm of PVB film/3 mm of glass can achieve a R_w of 33 dB, whereas 32 dB is the value measured for a monolithic pane of thickness 6 mm.

However, the insulation performance of known laminated safety glass is inadequate for many applications. When the sound insulation provided by laminated safety glass of the prior art, with a conventional PVB film as intermediate layer, is measured at room temperature the insulation rises steadily and approximately linearly within a wide range with increasing frequency, but a marked drop in insulation (relative minimum in insulation, coincidence drop) can be seen in particular in the frequency range from about 1000 to 3500 Hz. The position of this coincidence drop depends on the thickness of the glasses used. If each of the panes used has a thickness of 4 mm the coincidence drop is approximately in the range from 1 250 to 2 500 Hz, and if thinner panes are used the insulation drop shifts to higher frequencies, while the range is shifted toward lower frequencies if thicker panes are used. The term coincidence frequency is used below for the frequency at which the insulation curve passes through the relative minimum in the range of the coincidence drop.

Prior art

Proposals have previously been made for improving the sound insulation performance of laminated safety glass. US 5,773,102 (= EP 0 763 420 A1) discloses laminated safety glass in which a specific acoustic film is used,

besides a standard PVB film, to improve acoustic properties.

DE 197 05 586 C1 and EP 0 844 075 A1 likewise propose a thermoplastic intermediate layer itself having more than one layer, for a sound-insulating laminated pane of glass for motor vehicles. The laminate is composed of a viscoelastic acrylic polymer film, each side of which has been bonded via a polyethylene terephthalate film of from 0.01 to 0.1 mm thickness and a thermoplastic adhesive polyvinyl butyral film to two panes of silicate glass.
However, intermediate layers of this type which themselves have more than one layer involve complications in production, and frequently also in further processing.

Finally, DE 24 61 775 A1 discloses laminated safety glass in which, although the addition of very large amounts of standard plasticizer, in this case Flexol, achieves improved sound insulation, the amount of plasticizer used leads to increased tack, and the film therefore has limited capability for further processing using conventional systems.

Object

It is therefore an object of the present invention to provide, for laminated glass, an intermediate film which if possible has one layer and which is based on PVB, and which can give the laminated glass produced from the same improved sound insulation at room temperature, without any substantial alteration in ease of processing. A further object of the invention is to provide laminated glass having an intermediate layer based on PVB and providing improved sound insulation at room temperature.

Description of the invention

The invention achieves this object by means of laminated safety glass according to claim 1, preferably combined with one or more of the features of the subclaims, and, respectively, by means of a sound insulating film according to claim 7.

At the heart of the present invention is the use of a polyalkylene glycol of the formula $HO-(R-O)_n-H$ or derivatives of the same as a plasticizer, in addition to at least one first plasticizer known per se, in a PVB film.

Compared with conventional plasticizers, polyalkylene glycol or derivatives of the same used as coplasticizer in a PVB film bring about a marked improvement in sound insulation in laminated glass produced with a film of this type. In particular, the otherwise pronounced fall-off of sound insulation in the coincidence region is significantly less pronounced. Compared with a standard film composition, the proportion of polyvinyl butyral and/or of the standard plasticizer used in each case in the PVB film can be reduced and replaced by a polyalkylene glycol or a derivative of the same. The general embodiment of the invention is characterized by the fact that the polyalkylene glycol or, respectively, a derivative of the same, mixed with one or more conventional plasticizers, plasticizes the PVB resin.

In the general embodiment of the invention the total of the plasticizing components (polyalkylene glycol + conventional plasticizer) makes up from 20 to 50% by weight of the film. In its preferred embodiment the total plasticizer content is from 25 to 40% by weight and in the most preferred embodiment is from 30 to 35% by weight. The proportion of the polyalkylene glycol of the invention in the film here amounts to more than 5% by weight in the preferred case and to more than 10% by

weight in the most preferred case, in each case based on the total composition of the film.

For the purposes of the invention, polyalkylene glycols are those which have an average degree of polymerization DP of 6 or higher, but where this degree is not so high that combination with the other components of the film gives unacceptable haze in the laminated glass. Haze values which should be regarded as unacceptable when measured to ASTM D1003-6 are those above 3% haze or, respectively, ΔL deviations between greater than 3 found in comparative measurements of the duplex glass laminated with PVB film and duplex glass with no PVB film and taking $L_{(laminate)}-L_{(duplex\ glass)} = \Delta L$ in accordance with DIN 5033. The haze values are preferably below 1.5%, in particular below 1% haze for a film thickness of 0.76 mm.

For the purposes of the invention, the specific polyalkylene glycols may be poly(ethylene oxides), including block copolymers of the type $HO-(CH_2-CH_2-O)_n-(CH_2-CH(CH_3)-O)_m-H$, poly(propylene oxides) or poly-(butylene oxides), or else derivatives of the same, but poly(propylene oxides) are not preferred, since their effectiveness is low. The non-derivatized polyalkylene glycols of the invention should have an average degree of polymerization - referred to below as DP - of at least 6. Examples here are Pluriol® E 600 from BASF with an average degree of polymerization DP of 13.6 and Pluriol® P 2000 from BASF with an average degree of polymerization DP of 15.5.

For the purposes of the invention, derivatives of polyalkylene glycols are those in which the hydrogen of at least one of the two terminal hydroxyl groups of the polyalkylene glycol has been replaced by an organic radical. Possible examples here are ethoxylated fatty alcohols, ethoxylated fatty acids, such as the

polyethylene glycol ester of oleic acid, or monoethers of polyalkylene glycol with monohydric aliphatic alcohols, such as methanol or ethanol. Other examples are Marlophen® NP 6 from Condea, whose structure has a polyethylene glycol fraction with a DP of 6 and an isononylphenol fraction on one of the two hydroxyl-terminated ends, and also Marlipal® O 13/100 from Condea, whose structure has a polyethylene glycol fraction with a DP of 10 and a C_{13} oxo alcohol. In these monoderivatives of polyalkylene glycols, the DP of the polyalkylene glycol fraction must be at least 2. The upper DP limit is given by the compatibility with the other components of the film.

If the hydrogen of two terminal hydroxyl groups of the polyalkylene glycol fraction has been replaced by an organic radical, the polyalkylene glycol fraction must have a DP of at least 6. An example here is PEG-400 di(2-ethylhexanoate), a poly(ethylene glycol) di(2-ethylhexanoate), whose poly(ethylene glycol) fraction has an average molecular weight of 400 [g/mol].

The resins used in the novel film are partially acetalized polyvinyl alcohols known per se, in particular polyvinyl butyral. The partially acetalized polyvinyl alcohols are prepared in a known manner by acetalizing hydrolyzed polyvinyl esters. Examples of aldehydes which may be used are formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde and the like, preferably butyraldehyde. The preferred polyvinyl butyral resin contains from 10 to 25% by weight, preferably from 17 to 23% by weight and particularly preferably from 19 to 22% by weight, of vinyl alcohol radicals. The polyvinyl butyral may also, if desired, contain from 0 to 20% by weight, preferably from 0.5 to 2.5% by weight, of acetate radicals. Wherever the term polyvinyl butyral or PVB is used in this application it

generally also includes the other partially acetalized polyvinyl alcohols.

Besides the above-described polyalkylene glycols according to the invention, at least one further plasticizer is used. This is preferably a standard plasticizer selected from the group consisting of

- esters of polybasic aliphatic or aromatic acids, e.g. dialkyl adipates such as dihexyl adipate, dioctyl adipate, hexyl cyclohexyl adipate, mixtures of hepty and nonyl adipates, diisononyl adipate, heptyl nonyl adipate, and also esters of adipic acid with cycloaliphatic ester alcohols, dialkyl sebacates such as dibutyl sebacate, and phthalates such as butyl benzyl phthalate;
- esters of polyhydric aliphatic or aromatic alcohols or oligoether glycols having not more than four ethylene glycol units with one or more unbranched or branched aliphatic or aromatic substituents, e.g. esters of di-, tri- or tetraglycols with linear or branched aliphatic or cycloaliphatic carboxylic acids; Diethylene glycol bis(2-ethylhexanoate), triethylene glycol bis(2-ethylhexanoate), triethylene glycol bis(2-ethylbutanoate), tetraethylene glycol bis-n-heptanoate, triethylene glycol bis-n-heptanoate, and triethylene glycol bis-n-hexanoate can serve as examples of the latter group.

Particularly preferred standard plasticizers are di-n-hexyl adipate (DHA) and triethylene glycol bis-n-heptanoate (3G7).

To produce the novel PVB film with improved sound insulation, the liquid, paste or solid polyalkylene glycol component is mixed with the standard plasticizer, giving either a homogeneous solution of the polyalkylene glycol component in the plasticizer or, if the polyalkylene glycol component and

plasticizer are incompatible, a dispersion. The mixture made from plasticizer and polyalkylene glycol component is then processed together with the pulverulent polyvinyl butyral, while supplying heat and mechanical work, to give a homogeneous film mass, and this material is preferably extruded through a flat-film die to give a web of film. Further constituents which may, if desired, be present in the film are dyes, light stabilizers, stabilizers, processing aids, water, and also adhesion regulators.

The water content of the films is preferably set at from 0.15 to 0.8% by weight, in particular from 0.4 to 0.7% by weight.

Besides the improved insulation properties, the novel laminated safety glass (LSG) has the properties featured by LSG, such as resistance to breakage, splinter retention and transparency. For example, adhesion tests on the glass using a pummel test give values of 8-10 for the fire side and 7 for the tin side of the glass.

Methods of working the invention, and also comparative example

Example 1

22 parts by weight of triethylene glycol bis-n-heptanoate (3G7) as standard plasticizer, together with 11 parts by weight of Pluriol® 600, an unsubstituted poly(ethylene glycol) with an average molar mass of 600 [g/mol] or an average degree of polymerization DP of 13.6, and also 0.15 part by weight of Tinuvin® P UV absorber (manufacturer: Ciba) were added to 67 parts by weight of a polyvinyl butyral resin with a vinyl alcohol radical content (OH group content calculated as vinyl alcohol content) of 20.5% by weight and a vinyl acetate radical content of 0.7% by weight. The mixture was extruded at a melt

temperature of about 200°C in a twin-screw extruder with a flat-film die to give a transparent film of thickness 0.76 mm.

The PVB film and each of two panes of glass of dimensions 1480 × 1230 × 4 mm then underwent a lamination process, by simultaneous heating and compression in an autoclave, to give panes of laminated glass. The sound insulation value R_W of these panes was determined to DIN EN ISO 717 across the frequency band from 50 Hz to 5000 Hz at frequency intervals of one third of an octave. The temperature of the test specimen and of the test room was 21°C. Results of these measurements are shown in diagram 1 in the form of an insulation curve, in which higher values measured at a particular frequency signify better insulation.

Comparative example (example 2)

The insulation curve, shown for comparison in diagram 1, of laminated glass with the structure 4 mm of glass/0.76 mm of standard PVB/4 mm of glass, with 26% by weight of 3G7 as plasticizer, shows a clear drop in insulation between 1000 and 2000 Hz. This phenomenon is known as coincidence drop and represents a characteristic weakness - with respect to sound exclusion - of laminated glass produced with standard PVB.

The relative minimum in the sound insulation in the coincidence region is at about 1900 Hz, i.e. the coincidence frequency is 1900 Hz. At this frequency the insulation, at about 31.5 dB, is more than 5 dB below the corresponding value for the film according to example 1.

Examples 3 to 7

The examples 3 to 7 given in the table below were carried out as for example 1. The sound insulation curves for these examples 3 to 7 were at a level similar to the curve according to example 1.

Example/ constituent	1	2 (comparative)	3	4	5	6	7
Polyvinyl butyral	67	74	67	67	67	67	67
DHA[1]	-	-	-	22	-	22	22
3G7[2]	22	26	22	-	16.5		-
Pluriol® 600[3]	11	-	-	11	-		-
Marlophen® NP 12[4]	-	-	11	-	16.5		-
Marlophen® NP 6[5]	-	-	-	-	-		11
Poly-THF 650[6]						11	
UV absorber	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Property							
Film thickness [mm]	0.76	0.76	0.76	0.76	0.76	0.76	0.76
Haze ΔL	-0.32			0.01		0.26	-0.16
R_w[7]	37.0	35.4	36.4	37.3	36.1	36.2	36.9

(1) Di-n-hexyl adipate

(2) Triethylene glycol bis-n-heptanoate

(3) Poly(ethylene glycol) with an average molecular weight of 600 [g/mol]

(4) Monolaterally substituted PEG with a polyethylene glycol fraction with a DP of 12 and an isononylphenol fraction on one of the two hydroxyl-terminated ends.

(5) Bilaterally substituted PEG with a polyethylene glycol fraction with a DP of 6 and an isononylphenol fraction on one of the two hydroxyl-terminated ends.

(6) Polybutylene glycol with a DP of about 9 from BASF.

(7) Sound insulation value in dB measured to DIN EN ISO 717.

For all of the films of the examples the haze values found for the laminated glass were low and comparable with those for laminated glass laminated using a PVB film plasticized in a manner known per se. Despite the increased total plasticizer content, 33% by weight compared with 26% by weight in comparative example 2, there was no significant impairment of the handling properties of the film, in particular its tack. In comparison with this, a film with 33% by weight of 3G7 content would have a limited capability for further processing using conventional systems, due to high tack - as a result of plasticizer exudation.

Patent claims

1. Laminated safety glass, comprising
   - a first and a second pane of glass, and also,
   - arranged between the first and the second pane of glass, an intermediate layer, where the intermediate layer comprises:
     - from 50 to 80% by weight of PVB (partially acetalized polyvinyl alcohol)
     - from 20 to 50% by weight of a plasticizer mixture, comprising
       - from 30 to 70% by weight - calculated as proportion of the plasticizer mixture - of one or more polyalkylene glycols selected from the group consisting of
         - polyalkylene glycols of the general formula $HO-(R-O)_n-H$, where R = alkylene and $n > 5$,
         - block copolymers of ethylene glycol and propylene glycol having the general formula $HO-(CH_2-CH_2-O)_n-(CH_2-CH(CH_3)-O)_m-H$, where $n > 2$, $m > 3$, and $(n+m) < 25$,
         - derivatives of block copolymers of ethylene glycol and propylene glycol having the general formula $R_1O-(CH_2-CH_2-O)_n-(CH_2-CH(CH_3)-O)_m-H$ or $HO-(CH_2-CH_2-O)_n-(CH_2-CH(CH_3)-O)_m-R_1$, where $n > 2$, $m > 3$, and $(n+m) < 25$ and R_1 as organic radical,
         - derivatives of polyalkylene glycols of the general formula $R_1-O-(R_2-O)_n-H$, where R_2 = alkylene and $n \geq 2$, in which the hydrogen of one of the two terminal hydroxyl groups of the polyalkylene glycol has been replaced by an organic radical R_1,
         - derivatives of polyalkylene glycols of the general formula $R_1-O-(R_2-O)_n-R_3$, where R_2 = alkylene and $n > 5$, in which the

hydrogen of both terminal hydroxyl groups of the polyalkylene glycol has been replaced by an organic radical R_1 and, respectively, R_3.

2. Laminated safety glass according to claim 1, **characterized in that** the polyalkylene glycols have been selected from the group consisting of
- polyethylene glycol $HO-(CH_2-CH_2-O)_n-H$, where $8 < n < 25$,
- block copolymers of ethylene glycol and propylene glycol having the general formula $HO-(CH_2-CH_2-O)_n-(CH_2-CH(CH_3)-O)_m-H$, where $n > 3$, $m > 4$, and $(n+m) < 20$,
- derivatives of block copolymers of ethylene glycol and propylene glycol having the general formula $R_1O-(CH_2-CH_2-O)_n-(CH_2-CH(CH_3)-O)_m-H$ or $HO-(CH_2-CH_2-O)_n-(CH_2-CH(CH_3)-O)_m-R_1$, where $n > 3$, $m > 4$, and $(n+m) < 20$ and R_1 as organic radical,
- polybutylene glycol $HO-(CH_2-CH_2-CH_2-CH_2-O)_n-H$, where $4 < n < 18$,
- derivatives of the polyethylene glycol of the general formula $R_1-O-(CH_2-CH_2-O)_n-H$, where $n \geq 2$ and R_1 is an organic radical,
- derivatives of the polybutylene glycol of the general formula $R_1-O-(CH_2-CH_2-CH_2-CH_2-O)_n-H$, where $n \geq 2$ and R_1 is an organic radical.

3. Laminated safety glass according to claim 1 or 2, **characterized in that** the proportion of the polyalkylene glycols in the total mixture for the intermediate layer is greater than 10% by weight and less than 25% by weight.

4. Laminated safety glass according to any of claims 1 to 3, **characterized in that** at least one plasticizer selected from the group consisting of
- esters of polybasic aliphatic or aromatic acids,

- polyhydric aliphatic or aromatic alcohols or oligoether glycols having not more than four ether units with one or more unbranched or branched aliphatic or aromatic substituents, e.g. dialkyl adipate, dialkyl sebacate, esters of di-, tri- or tetraglycols with linear or branched aliphatic carboxylic acids

is used as further plasticizer in the plasticizer mixture.

5. Laminated safety glass according to claim 4, **characterized in that** at least one plasticizer selected from the group consisting of di-n-hexyl adipate (DHA) and triethylene glycol bis-n-heptanoate (3G7) is used as further plasticizer at a proportion > 10% by weight of the total mixture.

6. Laminated safety glass according to any of claims 1 to 5, **characterized in that** a polyvinyl butyral having from 19 to 22% by weight of vinyl alcohol radical and from 0.5 to 2.5% by weight of acetate radical is used as resin.

7. Sound-insulation film for producing laminated safety glass, comprising:

- from 50 to 80% by weight of PVB (partially acetalized polyvinyl alcohol),
- from 20 to 50% by weight of a plasticizer mixture, comprising
  - from 30 to 70% by weight - calculated as proportion of the plasticizer mixture - of one or more polyalkylene glycols selected from the group consisting of
    - polyalkylene glycols of the general formula $HO-(R-O)_n-H$, where R = alkylene and n > 5,
    - block copolymers of ethylene glycol and propylene glycol having the general

formula $HO-(CH_2-CH_2-O)_n-(CH_2-CH(CH_3)-O)_m-H$, where $n > 2$, $m > 3$, and $(n+m) < 25$,

- derivatives of block copolymers of ethylene glycol and propylene glycol having the general formula $R_1O-(CH_2-CH_2-O)_n-(CH_2-CH(CH_3)-O)_m-H$ or $HO-(CH_2-CH_2-O)_n-(CH_2-CH(CH_3)-O)_m-R_1$, where $n > 2$, $m > 3$, and $(n+m) < 25$ and R_1 as organic radical,
- derivatives of polyalkylene glycols of the general formula $R_1-O-(R_2-O)_n-H$, where R_2 = alkylene and $n \geq 2$, in which the hydrogen of one of the two terminal hydroxyl groups of the polyalkylene glycol has been replaced by an organic radical R_1,
- derivatives of polyalkylene glycols of the general formula $R_1-O-(R_2-O)_n-R_3$, where R_2 = alkylene and $n > 5$, in which the hydrogen of both terminal hydroxyl groups of the polyalkylene glycol has been replaced by an organic radical R_1 and, respectively, R_3.

8. Use of one or more polyalkylene glycols selected from the group consisting of

- polyalkylene glycols of the general formula $HO-(R-O)_n-H$, where R = alkylene and $n > 5$,
- block copolymers of ethylene glycol and propylene glycol having the general formula $HO-(CH_2-CH_2-O)_n-(CH_2-CH(CH_3)-O)_m-H$, where $n > 2$, $m > 3$, and $(n+m) < 25$,
- derivatives of block copolymers of ethylene glycol and propylene glycol having the general formula $R_1O-(CH_2-CH_2-O)_n-(CH_2-CH(CH_3)-O)_m-H$ or $HO-(CH_2-CH_2-O)_n-(CH_2-CH(CH_3)-O)_m-R_1$, where $n > 2$, $m > 3$, and $(n+m) < 25$ and R_1 as organic radical,
- derivatives of polyalkylene glycols of the general formula $R_1-O-(R_2-O)_n-H$, where

R_2 = alkylene and $n \geq 2$, in which the hydrogen of one of the two terminal hydroxyl groups of the polyalkylene glycol has been replaced by an organic radical R_1,

- derivatives of polyalkylene glycols of the general formula $R_1\text{-}O\text{-}(R_2\text{-}O)_n\text{-}R_3$, where R_2 = alkylene and $n > 5$, in which the hydrogen of both terminal hydroxyl groups of the polyalkylene glycol has been replaced by an organic radical R_1 and, respectively, R_3,

as an additive improving sound insulation in films produced from plasticized PVB resin for laminated safety glass, where the sound insulation of the laminated safety glass is increased by the addition of the polyalkylene glycols by at least 2 dB, measured to DIN EN ISO 717, in the coincidence frequency region from 1000 to 3500 Hz.

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

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[Fortsetzung auf der nächsten Seite]

(54) **Title:** COMPOUND SAFETY GLASS AND PVB FOIL FOR THE PRODUCTION THEREOF

(54) **Bezeichnung:** VERBUNDSICHERHEITSGLAS SOWIE PVB-FOLIE ZU SEINER HERSTELLUNG

(57) **Abstract:** Known intermediate foils for compound glasses with improved sound insulation consist of several layers or special materials which cannot be further processed in conventional plants. The aim of the present invention is to provide an intermediate foil for compound glasses with improved sound insulation, whereby said foil consists of one layer as far as possible and is based upon PVB. Said intermediate foil allows for an improved sound insulation of the compound glasses in room temperature and has essentially unchanged working properties, whereby said compound glasses are produced from the intermediate foil. To resolve the aim of the invention, an intermediate foil is provided which contains: 50 to 80 wt. % PVB (partially acetalised polyvinyl alcohol), 20 to 50 wt. % of a softener mixture containing 30 to 70 wt. %, calculated as a portion of the softener mixture, of one or more polyalkylene glycoles of the group consisting of polyalkylene glykoles of the general formula HO-(R-O)n-H with R = alkylene and n > 5, block copolymers made of ethylene- and propylene glycole of the general formula HO-(CH2-CH2-O)n-(CH2-CH(CH3)-O)m-H with n > 2, m > 3 and (n+m) < 25, derivatives of block copolymers made of ethylene- and propylene glycole of the general formula R1O-(CH2-CH2-O)n-(CH2-CH(CH3)-O)m-H or HO-(CH2-CH2-O)n-(CH2-CH(CH3)-O)m-R1 with n > 2, m > 3 and (n+m) < 25 and R1 as the organic radical, derivatives of polyalkylene glycols of the general formula R1-O-(R2-O)n-H with R2 = alkylene and n > 2, wherein the hydrogen of one of the two terminal hydroxygroups of the polyalkylene glycol is replaced by an organic Rest R1, derivatives of polyalkylene glycols of the general formula R1-O-(R2-O)n-R3 with R2 = alkylene and n > 5, wherein the hydrogen of the two terminal hydroxygroups of the polyalkylene glycol is replaced by an organic Rest R1 or R3.

(57) **Zusammenfassung:** Bekannte Zwischenfolien für Verbundgläser mit verbesserter Schalldämmung sind entweder mehrschichtig aufgebaut oder aus besonderen Materialien gefertigt, die sich nicht in üblichen Anlagen weiterverarbeiten lassen. Aufgabe der vorliegenden Erfindung ist es, eine möglichst einschichtige Zwischenfolie für Verbundgläser mit verbesserter Schalldämmung auf der Basis von PVB zur Verfügung zu stellen, die bei weitgehend unveränderter Verarbeitbarkeit eine bei Raumtemperatur verbesserte Schalldämmung der daraus hergestellten Verbundgläser ermöglicht. Hierzu schlägt die Erfindung eine Zwischenfolie vor, enthaltend: 50 bis 80 Gew.-% PVB (teilacetalisierter Polyvinylalkohol); 20 bis 50 Gew.-% einer Weichmachermischung, enthaltend; 30 bis 70 Gew.-% - gerechnet als Anteil an der Weichmachermischung - eines oder mehrerer Polyalkylenglykole der Gruppe bestehend aus; Polyalkylenglykolen der allgemeinen Formel HO-(R-O)n-H mit R = Alkylen und n > 5; Blockcopolymeren aus Ethylen- und Propylenglykol der allgemeinen Formel HO-(CH2-CH2-O)n-(CH2-CH(CH3)-O)m-H mit n > 2, m > 3 und (n+m) < 25; Derivaten von Blockcopolymeren aus Ethylen- und Propylenglykol der allgemeinen Formel R1O-(CH2-CH2-O)n-(CH2-CH(CH3)-O)m-H bzw. HO-(CH2-CH2-O)n-(CH2-CH(CH3)-O)m-R1 mit n > 2, m > 3 und (n+m) < 25 und R1 als organischem Rest; Derivate von Polyalkylenglykolen der allgemeinen Formel R1-O-(R2-O)n-H mit R2 = Alkylen und n > 2, bei denen der Wasserstoff von einer der beiden terminalen Hydroxygruppen des Polyalkylenglykols durch einen organischen Rest R1 ersetzt ist; Derivate von Polyalkylenglykolen der allgemeinen Formel R1-O-(R2-O)n-R3 mit R2 = Alkylen und n > 5, bei denen der Wasserstoff von beiden terminalen Hydroxygruppen des Polyalkylenglykols durch einen organischen Rest R1 bzw. R3 ersetzt ist.

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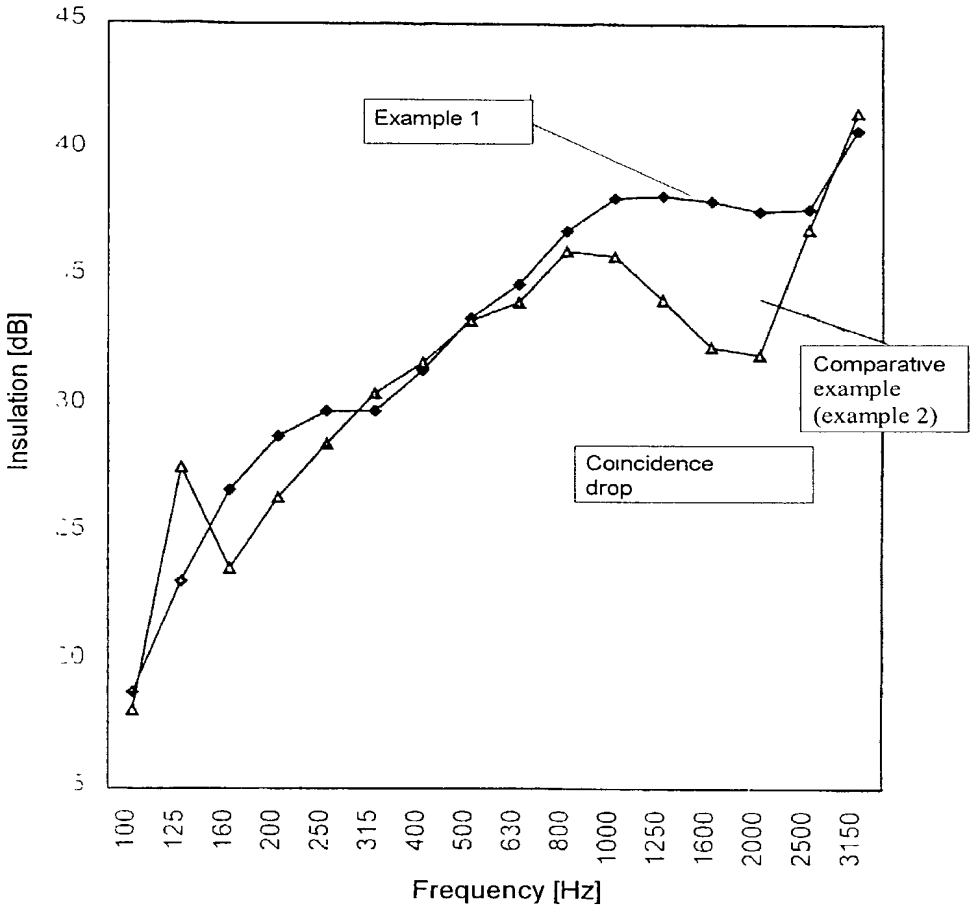
Diagram 1


45
40
35
30
25
20
Insulation [dB]
Example 1
Comparative example (example 2)
Coincidence drop
100
125
160
200
250
315
400
500
630
800
1000
1250
1600
2000
2500
3150
Frequency [Hz]

Attorney Docket Number: TROPL12

DECLARATION FOR PATENT APPLICATION

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

COMPOUND SAFETY GLASS AND PVB FOIL FOR THE PRODUCTION THEROF

the specification of which

- ☐ is attached hereto
- ■ was filed on 16 AUGUST 2000 as United States Application Number or PCT International Application Number PCT/DE00/02743 and (if applicable) was amended on _____

I hereby authorize our attorneys to insert the serial number assigned to this application.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR §1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 USC §119			
APPLICATION NO.	COUNTRY	DAY/MONTH/YEAR FILED	PRIORITY CLAIMED
199 38 159.3	GERMANY	16 AUGUST 1999	YES

I hereby claim the benefit under 35 U.S.C. §119(e) of any United States provisional application(s) listed below.

PROVISIONAL APPLICATION(S) UNDER 35 U.S.C. §119(e)	
APPLICATION NUMBER	FILING DATE

I hereby claim the benefit under 35 U.S.C. §120 of any United States application, or §365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. §112.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR §1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

PRIOR U.S./PCT INTERNATIONAL APPLICATION(S) DESIGNATED FOR BENEFIT UNDER 37 U.S.C. §120		
APPLICATION NO.	FILING DATE	STATUS — PATENTED, PENDING, ABANDONED

I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected herewith: I. William Millen (19,544); John L. White (17,746); Anthony J. Zelano (27,969); Alan E.J. Branigan (20,565); John R. Moses (24,983); Harry B. Shubin (32,004); Brion P. Heaney (32,542); Richard J. Traverso (30,595); John A. Sopp (33,103); Richard M. Lebovitz (37,067); John H. Thomas (33,460); Catherine M. Joyce (40,668); Nancy J. Axelrod (44,014); James T. Moore (35,619); James E. Ruland (37,432); Jennifer J. Branigan (40,921) and Robert E. McCarthy (46,044)

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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☐ Additional joint inventors are named on separately numbered sheets attached hereto.